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TEXTURAL PROPERTIES OF MACROPOROUS ACID MODIFIED MONTMORILLONITE NANOCOMPOSITES

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Abstract

Macroporous crosslinked copolymer, poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) and its nanocomposites with acid modified montmorillonite (W_A) were synthesized by radical suspension copolymerization. Nanocomposites were obtained by introducing various amounts of W_A into the reaction system. Textural properties of synthesized samples were analyzed by mercury intrusion porosimetry. The synthesized nanocomposites have significantly higher specific surface area in comparison to the copolymer. Total pore volume and the most dominant pore diameter decrease with incorporation of acid modified montmorillonite in copolymer matrix.

Introduction

The study of polymer/clay nanocomposites is currently an expanding field of research because polymer/clay nanocomposites often exhibit a wide range of improved properties over their unmodified starting polymers. The improved properties for these nanocomposites include mechanical, thermal, flammability [1], and textural properties [2,3] and are related to the dispersion and nanostructure of the layered silicate in the polymer.

To our knowledge, we were the first to report the preparation of porous polymer/clay nanocomposites of poly(GMA-*co*-EGDMA) by radical suspension copolymerization [2,3]. Porous materials have numerous applications in such areas as catalysis, chromatography and separation, where control over pore structure and pore size strongly influences the efficiency of the material [4]. Since the application of the obtained nanocomposites strongly depends on its textural properties the goal of the present work was mainly to study the effect of acid modified montmorillonite incorporation on the porous structure of poly(GMA-*co*-EGDMA) based nanocomposites.

The influence of the amount of acid modified montmorillonite introduced into the reaction mixture on the tailoring of textural properties of poly(GMA-*co*-EGDMA) based nanocomposites was investigated.

Experimental

Starting material for acid modification was Wyoming type Na-montmorillonite (Clay Minerals Society Source Clay). Acid modification was performed with 3 M HCl at 90 °C for 2 h. The liquid (acid solution)/ solid (clay) ratio was 4:1. After modification, the clay suspension was filtrated under vacuum. The filtration cake was rinsed with deionized water at 80 °C until the filtrate was Cl^- and/or Fe^{3+} free. After drying to constant mass at 110 °C acid modified clay was reground to pass through a 74 µm sieve and denoted W_A [2,3]. Macroporous crosslinked copolymer, poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) was synthesized by suspension copolymerization in manner that was previously reported [5] and denoted as CP. Nanocomposites were obtained in same manner as CP, only 2.5, 5, 10 mass % of acid modified montmorillonite was introduced into reaction system [2, 3]. The obtained nanocomposites in form of regular spheres (0.15 mm $<d<$ 0.30 mm) were denoted CP-2.5W_A, CP-5W_A and CP-10W_A. The porous structure of samples was determined using Carlo Erba Porosimeter 2000 with Milestone 100 Software System. The specific surface area of samples (S_{Hg}), total pore volume (V_p) and the most dominant diameter in macroporous region (d_{max}) were determined from cumulative pore size distribution curves [6]. Pores have commonly irregular shape and the most similar geometric form is used to represent pore shape [7]. For investigated materials the cylindrical shape is assumed for calculation of textural properties [2, 5].

Results and Discussion

Results obtained by mercury intrusion porosimetry for copolymer and nanocomposites are given in Fig. 1 and Table 1.

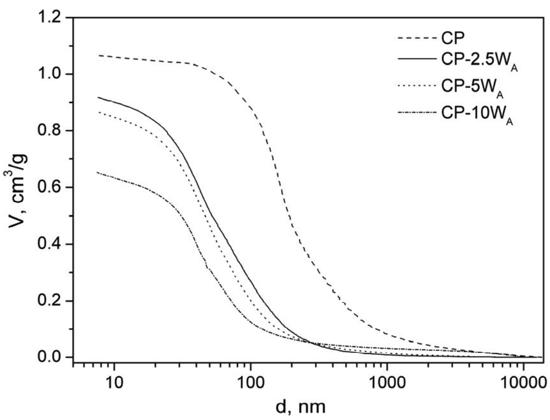

Figure 1. Cumulative pore size distribution curves of the copolymer and nanocomposites with varied amount of acid modified montmorillonite

By comparison of the results obtained for the copolymer and the nanocomposites it can be concluded that all textural properties were affected by the incorporation of the acid modified montmorillonite. The cumulative pore size distribution curve for the copolymer has a plateau in the area of mesopores (<50 nm). On the other hand, the curves for all nanocomposites have a constant increase in the mesoporous area instead of a plateau suggesting the presence of pores <7.5 nm.

Table 1. Porosity parameters of copolymer and nanocomposites.

Sample	S_{Hg} m^2g^{-1}	V_p cm^3g^{-1}	d_{max} nm
CP	33	1.06	170
CP-2.5W_A	88	0.92	58
CP-5W_A	84	0.87	53
CP-10W_A	73	0.66	47

The pore diameter of the nanocomposites shifted toward pores with smaller pore diameters, falling entirely below 200 nm.

Also, a significant increase of specific surface area (almost three times) of the nanocomposites in comparison to the copolymer was obtained.On the other hand, difference in textural properties between nanocomposites with varied amount of incorporated acid modified montmorillonite was less expressed. The values of S_{Hg}, V_p and d_{max} of the nanocomposites slightly decreased with the increase of the amount of introduced W_A.

Conclusion

Macroporous crosslinked copolymer poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) and its nanocomposites with different amounts of acid modified Na-montmorillonite originated from Wyoming (W_A) were synthesized by radical suspension copolymerization. The formation of nanocomposites strongly affected all textural properties. The incorporation of clay filer into copolymer lead to materials with slightly smaller total pore volume but almost three times increased specific surface area in comparison to the copolymer. The difference in textural properties between nanocomposites with varied amount of incorporated acid modified montmorillonite was less expressed.

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